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MANUFACTURE OF SCOURING CLEANSER
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11 Claims

ABSTRACT OF THE DISCLOSURE

Scouring cleansers are made by neutralization of a detergent acid with an excess of calcium carbonate, whereby a calcium-detergent salt is produced together with calcium carbonate scouring material. Such cleansers have improved foaming power and bleaches present in them are more stable on storage than in similar products containing a corresponding sodium-detergent salt.

This invention relates to scouring cleansers. More particularly, it is of a method for making a scouring cleanser by dry neutralization of a detergent acid with an excess of calcium carbonate, whereby calcium detergent is produced, together with calcium carbonate scouring material. The scouring cleansers made have been found to be of improved foaming power and bleaches present in them are more stable on storage than in similar products in which the calcium detergent salt is replaced by a corresponding sodium detergent salt.

Scouring cleansers comprise major proportions of water insoluble particulate or pulverulent materials, usually silica or silex, with minor proportions of organic cleaning material, such as soap or synthetic organic detergent (which may also function as a foaming agent), and perfume. Bleaching materials have been added to such compositions to aid in the removal of stains from the surfaces being scoured, which are usually of porcelain, tile or stoneware, e.g., sinks or tubs. In some cases, inorganic builders, fillers, alkalis, acids or buffers may be used to give the scouring cleansers additional characteristics or to improve properties thereof.

In the United States the prevalent scouring material at the present is silex. The detergent component of scouring cleansers is usually made by neutralization of a detergent acid by an alkali metal hydroxide base. Generally, the neutralization occurs in an aqueous medium in which the acid and base are dissolved or dispersed. Thus, a detergent acid made by the sulfonation of alkyl benzene by oleum or sulfur trioxide may be neutralized with a sodium hydroxide solution. When water is the solvent, this leaves too much water present with the neutral detergent so that if it is mixed with a water insoluble scouring material too much lumping could occur and it could tend to cake on storage. To remove the water, the neutralized detergent, usually with additional builder salts or carriers to improve drying and flow properties, is spray dried to bead form and the free flowing beads produced are blended with abrasive to yield a scouring powder. In some cases, after the blending the mixture is put through a size-reducing machine, such as an impact strip or hammer mill of the micropulverizer or Entoliter types. This helps to distribute further the various components of the scouring powder and makes the particle sizes more uniform and finer. Instead of spray drying, drum drying, pan drying, flash drying, film drying, hydration and other techniques may be used, either to remove the water or to tie it up so as to make it less of a problem in the scouring cleanser formulations.

The prior art has recognized that a dry neutralization process, if practicable, would usually be cheaper than a combination wet neutralization and spray drying process,

and although some dry neutralizations have been carried out, no previous description is known of a process in which the neutralization is effected by use of a large excess of calcium carbonate neutralizing agent and the neutralized detergent, dispersed in the excess of such agent, is then directly useful as a scouring cleanser or may be employed in combination with additive or adjuvant materials. For example, in a comparable reaction, if an excess of sodium carbonate is used, the excess, while it may be useful as a builder or alkalizer, is not an active scouring material. Therefore, the formulations must be further modified or the additional expense thereof must be absorbed. In the present compositions, the calcium carbonate neutralizing agent not consumed is directly useful as an active ingredient of the scouring cleansers to be made. Furthermore, it has been found that smaller proportions of calcium detergent are as effective in cleaning and foaming in the present cleansers as are larger proportions of corresponding sodium detergents. This allows savings to be made in the formulation and, because of the presence of lesser amounts of synthetic organic detergent, makes the scouring cleanser more freely flowable and less liable to become tacky or to lump on storage. Such a result is surprising since it has long been considered that sodium detergents, as a rule, are superior in foaming and cleaning power to those based on alkaline earth metal, heavier metal and heavy metal salts. Another significant advantage of the present compositions, produced by the described method, is in the discovery of greater stabilities of formulations containing bleaches, such as the chlorinated bleaches, specifically, those based on chlorocyanuric acids. While the invention is of special importance in conjunction with the manufacture of scouring cleansers, it is also useful to make calcium salts of detergent acids for other end applications.

In accordance with the present invention, a process for the manufacture of a scouring cleanser comprising a substantially water-insoluble scouring material and a synthetic organic detergent salt comprises neutralizing an essentially dry acid form of the synthetic organic detergent component with a large excess of powdered calcium carbonate in the presence of a minor proportion of water on loci of contacts of the detergent acid and calcium carbonate powder. In specific embodiments of the invention the synthetic organic detergent acid will be a liquid, higher alkyl benzene sulfonic acid, the scouring cleanser scouring material will be calcium carbonate, water will be sprayed in while the detergent acid and the carbonate are being mixed, hydratable salt, bleaching material and perfume will be added after the neutralization and the product will be size reduced, usually by an impact mill.

Also within the invention are scouring cleanser compositions comprising a water insoluble scouring material, including at least 25% calcium carbonate, a foaming calcium salt of a synthetic organic detergent acid and water, preferably with a chlorine releasing bleaching compound present which is stable in such a product.

The detergent acids are normally water soluble and are in liquid form, preferably being obtained by settling out of an aqueous solution of reaction products resulting from a reaction by which the acid is produced. Other detergents may be present, such as nonionic and amphoteric or ampholytic detergents but the acid being neutralized will usually be that of an anionic detergent. Nevertheless, it should be apparent that acids of other surface active agents, foaming compounds and hydro-tropes, for use in detergent or scouring cleanser compositions, may also be neutralized by the present method, preferably in mixture with the detergent acid.

Of the anionic detergents the method is applicable broadly whenever neutralization of the acid radical can

be effected with a weak base, such as calcium carbonate. Thus, higher fatty acid monoglyceride sulfates, higher fatty acid amides of N-methyl taurine, higher fatty alcohol sulfates, higher fatty alcohol sulfonates, olefin sulfonates, phenyl polyoxyethylene sulfates, middle alkyl phenoxy polyethoxy sulfates, aryl higher alkyl sulfonates and higher alkyl aryl sulfonates may be neutralized. By higher alkyl is meant an alkyl radical, branched or linear, of from 12 to 18 carbon atoms and by middle alkyl is meant alkyl of 7 to 9 carbon atoms. Higher fatty acids are those of 12 to 18 carbon atoms and include unsaturated acids having a double bond. The poly-lower alkoxy chains mentioned are usually from 3 to 20 alkoxies long.

Of the water soluble anionic detergent acids, the higher alkyl aryl sulfonic acids are preferred, wherein the aryl may be benzene, naphthalene or such nuclei substituted with up to three radicals selected from the group consisting of lower alkyl (of 1 to 4 carbon atoms), halogen (including chlorine and bromine), amino, nitro, hydroxy and lower alkoxy. Although solid detergents may be used, preferably in particulate or powder form, generally the detergent will be in the liquid state, present with a very small proportion of water. As was indicative above, it is preferred to utilize the detergent or upper layer of a settled out sulfonation product wherein higher alkyl benzene, often called alkylate, is sulfonated with oleum or sulfur trioxide. Although the upper layer may be considered to be the non-aqueous layer of such a separation, the material does disperse fairly well in aqueous solutions, especially if an auxiliary solvent or a base is present, and it is readily reactive with aqueous bases or with bases when moisture is present. The higher alkyls may be linear, in which case they are usually joined to the benzene ring at the 1- or 2-carbon of the alkyl chain, or they may be highly branched, such as those obtained by polymerization of a lower alkene, such as propylene. Preferably they are of 12 to 15 carbon atoms and most preferably, of 12 to 13 carbon atoms. Although the propylene tetramer alkyl benzene sulfonates are found to be more difficultly biodegradable than the linear alkyl benzene sulfonates, where such a consideration is not considered to be of sufficient importance to warrant use of only the linear compounds it has been found that branched chain detergents are readily manufactured and give very satisfactory scouring cleansers of good foaming power, and bleach stability, when a halogenated bleach is present. However, for best flowability of the neutralized detergent and the scouring cleanser made with it the linear alkyl benzene sulfonates are preferred.

The usual embodiment of the present invention is that in which an alkyl benzene sulfonate of the type described, without any other materials present with it except for the byproducts of the sulfonation reaction, is neutralized with calcium carbonate in the presence of small amount of water sprayed onto the moving mixture. Yet, where desired, other materials may be present with the liquid detergent acid, such as solvents, e.g., ethanol, isopropanol; hydrotropes; foaming agents; and inorganic non-reactive salts, e.g., sodium sulfate, sodium chloride. However, the proportions of such adjuvant materials will generally be limited to no more than 50% of the alkyl benzene sulfonic acid content and preferably, will be less than 10% thereof. Other materials that will usually be present with the alkyl benzene sulfonic acid include water, generally from 0.1 to 5%, and sulfuric acid, generally from 0.1 to 10%. Additionally present may be from 0.5 to 3% of free oil, usually alkane or alkyl benzene. The content of higher alkyl benzene sulfonic acid in the acid charge usually employed will generally be from 85 to 98%, the higher contents, 92 to 98%, being from products manufactured by sulfonation with sulfur trioxide and the lower contents, from 85 to 92% being from sulfonations with oleum or fuming sulfuric acid.

Of course, in both cases the product used is that which has been water washed and well settled. As a result of the

water washing and the use of an aqueous medium for neutralization, the upper layer detergent acid, although essentially dry, can contain as much as about 10% of water. Usually the water content will be less and many times will be in the range of a trace or 0.1%, to 3 or 5%. Of course, if after a good separation of the detergent acid from the aqueous phase is obtained it is desired to increase the moisture content of the acid, this can be done but even under such circumstances the moisture content of the detergent acid will rarely be in excess of 20%, to avoid undue lumping in the neutralization reaction. Preferably, the total moisture content of the finished product, either free or tied up as water of hydration, will be no more than about 5%. The sulfuric acid content of the upper layer of detergent acid should usually be minimized to as little as feasible to avoid expending calcium carbonate in producing calcium sulfate, together with gaseous carbon dioxide byproduct. However, in some products it will be desirable to have calcium sulfate present and in some processes the production of gas may be useful to keep the reaction mixture in motion. Under such circumstances, the sulfuric acid content may be greater than the previously described limits and extra sulfuric acid or other acid may be intentionally added. Normally though, it will be desirable to have the detergent acid at as high a concentration as feasible with the water content being in the 0.1 to 5% range and the sulfuric acid content being minimal. Similarly, it would usually be preferred to maintain the free oil content as low as possible.

The calcium carbonate employed to neutralize the detergent acid will preferably be ground limestone, chalk or calcite, of a particle size sufficiently small so that it does not scratch. However, the particles should be large enough so as to possess significant cleaning power. Often the particle sizes will be such that substantially all of the calcium carbonate will pass through a 200-mesh sieve. By "substantially all" is meant over about 98% of the particles, by weight. Yet, good scouring cleansers have been made in which the particles don't all pass a 200 mesh sieve but do clear a 140 mesh sieve. It is highly desirable that finished product should substantially pass through a 140 mesh sieve, thereby indicating more than 90%, by weight, thereof being of a particle size of approximately 100 microns or less. Instead of charging a very finely divided calcium carbonate to the neutralizer, a coarser powder may be utilized at this stage and it may subsequently be ground or impact size reduced to under about 100 microns or to pass a 200 mesh sieve, if a finer product is desired. Yet, to get quickest neutralization it will be preferable to charge the more finely divided calcium carbonate to the mixer. The calcium carbonate, as charged, will have a very low moisture content, generally only a trace to 1%, and anhydrous powder is preferred. If desired, other neutralizing agents may be mixed with the calcium carbonate, such as other salts, oxides or hydroxides, and in some circumstances such mixing may be obtained by utilizing a mixed salt mineral as the source of the calcium carbonate, e.g., dolomite.

In addition to the detergent acid and calcium carbonate, the only other constituent of the present composition, in its broad aspect, and an important reactant in the broad processes of the invention is water. This will normally be deionized water but distilled water and tap waters of hardnesses up to 150 parts per million may be usually employed, as may even harder waters in appropriate circumstances. The water may be present in the detergent acid or in the calcium carbonate but it has been found that water so contained is not as effective in aiding the present neutralization as is water sprayed onto the reactants while they are being tumbled, as in a ribbon mixer. Such spraying has the water contact the various small particles of solid calcium carbonate and subsequent contact with detergent acid leads to quick neutralization. For best action, the water should be atomized so that the particles thereof are small, usually averaging in the range

of from 5 to 100 microns in diameter. Streams or sprays of water may also be employed but at a loss in efficiency of the neutralization process. Such streams or sprays will normally and preferably be utilized for the detergent acid because of the desirability of preventing such acid, in very finely divided globular form from being carried out of the mixer and lost. Thus, if fairly finely divided sprays are utilized, the droplets will preferably be in the upper portion of the particle size range given for the water globules, e.g. 50 to 100 microns. In either case, the reaction will be expedited at the loci of contacts between the detergent acid and the calcium carbonate when water has been brought to such loci and is on the surfaces thereof shortly before, after or at the same time at which the contacts are effected.

Various useful builder and filler salts may be present in the final product. Normally, these are added subsequent to the neutralization being completed. The salts are preferably hydratable so that they may take up moisture from the neutralize reaction mixture, thereby making the product more readily flowable and minimizing lumping and caking on storage. Various hydratable builder salts may be employed, including the alkali metal polyphosphates, e.g., tetrapotassium pyrophosphate, pentasodium tripoly phosphate, trisodium phosphate and sodium hydrogen phosphate. Generally, sodium salts will be preferred but other alkali metal and alkaline earth metal soluble salts may also be used. In some cases, insoluble alkaline earth and heavy metal salts may be desirable components of the products. In the present composition the trisodium phosphate has been found to act as a good cleaning agent, alkaliizer and water sorber and is most preferred.

In modern scouring cleansers and many other detergent compositions bleaching action is desirable and for this purpose there is included in such products a source of oxygen, chlorine or bromine, the most common bleaching materials employed. Various sources of oxygen may be utilized, including hypochlorites and percompounds, e.g., sodium perborate, and catalysts, e.g., ammonium molybdate, may be present or added to accelerate the decomposition of such products upon use. Sources of chlorine and bromine include chlorophosphates, hypochlorites, chlorinated cyanuric acids and oxidizable chlorides. Similarly, with respect to bromine, hypobromites and bromides, e.g., sodium bromide, may be employed. Of the bleaches, those most preferred in the present composition and processes and those which have been found to be significantly stabilized by the compositions containing calcium detergent salt are the chlorinated cyanuric acids, e.g., trichlorocyanuric and dichloroisocyanuric acids. These are in powder form, are sufficiently stable on storage, and quickly release their bleaching agents when the scouring cleanser is utilized in conjunction with water.

Various adjuvants may be included in the formulation. Although these are preferably added after completion of neutralization, in certain cases it may be desirable to premix them with either the detergent acid, the calcium carbonate or the water being atomized onto the moving reactants. Certainly, if they are to be added in the mixer before or during neutralization they should be non-interfering with the reaction and should not be adversely affected by contact with the reagents. Among the adjuvants that may be employed are reducing agents, perfumes, colorants, bactericides, fungicides, foaming agents, solvents, brighteners, enzymes, bulking materials, buffers, pH modifiers, stabilizers, soil dispersants and sequestrants. Agents may be employed for assisting in conversion of calcium detergent salts to more soluble alkali metal detergent salts, when the scouring cleanser is being used. In addition to incorporating the adjuvants after neutralization and before size-reduction, they may also be added after size reduction, providing that they are of such sizes initially as to blend well with the size-reduced scouring cleanser ingredients.

With the exception of the adjuvants, which would

usually comprise a minor proportion, generally less than 5% each and preferably less than 2% each of the product, most preferably less than 1% each, with a total adjuvant content less than 20%, preferably less than 10% and most preferably less than 5% of the composition, the proportions of the reagents and other highly preferred components of the products will be those set forth below and elsewhere in this specification.

The neutralizing agent, calcium carbonate, will be used in large excess of the amount required to react with the detergent acid. Therefore, the product after neutralization will usually be essentially calcium carbonate, with small proportions of the detergent salt and other materials that also may be present.

The substantially water insoluble scouring material, dissolving to the extent of less than about 1% in water at approximately room temperature, is used in large excess, being from about 500 to 20,000 percent by weight of the detergent acid employed. If desired, other inert scouring materials may be used with the calcium carbonate or suitable reactive "abrasive" component. In preferred embodiments of the invention, usually wherein the calcium carbonate is the sole scouring, abrasive or polishing material, the excess thereof employed, with respect to the detergent acid, will be from 1,000 to 5,000 percent. Desirably, the calcium carbonate should comprise at least 20%, preferably 50% and most preferably from 85 to 98% of the neutralized scouring cleanser. The detergent acid and the calcium detergent made from it will usually be from 0.5 to 5% of the cleanser, preferably from 2 to 4% thereof. Because the molecular weight of the anionic portion of the detergent is high, no distinction is made between the acid salt forms with respect to such percentages although, as is clear, the percentage of salt will be greater than that of the corresponding acid. The water sprayed onto the contact loci will be a minor proportion of the product, usually from 0.1 to 5% thereof, preferably from 0.1 to 3% and most preferably from 0.1 to 0.5%. The trisodium phosphate or other hydratable builder salt will be from 1 to 5% of the product, preferably about 3% thereof, the bleaching agent, preferably trichlorocyanuric acid, will be from 0.1 to 2%, preferably from 0.2 to 0.5%, the perfume will constitute from about 0.05 to 1%, preferably from 0.1 to 1%, and the final moisture content of the product will be from about 0.1 to 5%, preferably from 0.4 to 3%. In the best embodiments of the invention, wherein the detergent is calcium salt of propylene tetramer benzene sulfonic acid or corresponding linear tridecyl benzene sulfonic acid and trisodium phosphate, trichlorocyanuric acid, perfume and water are present in the product, the calcium carbonate scouring material comprises over 90% of the product. Such a cleanser is directly useful after manufacture but in some embodiments may be mixed with other materials or may be employed not as a scouring cleanser but as a laundry detergent or hard surface cleanser.

The production of scouring cleansers or detergents by means of the present method is comparatively simple and requires no unusual apparatuses. It does not cause any significant increase in the time required for the manufacture of scouring cleansers. All that are needed are feeding mechanisms for supplying the reagents and other components of the detergent composition to a mixer, plus a grinder or other size-reducing machine. The product may be seen to storage after grinding, without any screening being necessary or it may be directly filled into cans or packages. Because of the simplicity of the operational steps for making products according to this invention it is considered that no drawing is necessary to illustrate them.

In carrying out the invented process, well settled detergent acid is fed onto a moving base of calcium carbonate in a suitable mixer. Ribbon mixers are useful but other mixing devices, such as the Lodge high velocity mixers, twin shell blenders, preferably equipped with breaker bars (Patterson-Kelly), powder blenders, Sigma blade mixers

and other well known types may also be utilized. The temperature of the mixer and the reactants may be regulated by heating means therein to be at a desired temperature within the range of 0 to 70° C. but normally the reaction will take place at approximately room temperature, e.g., 10° C. to 40° C. preferably from 20 to 35° C. In most cases heating or cooling will not be necessary because of the large quantity of calcium carbonate normally present to absorb the heat of reaction. The base of calcium carbonate in the mixer initially will usually be from 10 to 40% of the entire charge of the scouring material. The detergent acid and the rest of the calcium carbonate will then be added to the operating mixer together and inside the mixer water will be sprayed onto the moving particles to create reaction loci. The addition of all the materials and the reaction to produce the neutralized detergent will usually be completed within about 15 minutes, preferably within 10 minutes or less. Normally, the admixing should be effectable within 5 to 10 minutes during which time or after completion of the mixing, spraying with water may be effected within a five minute period and neutralization will be substantially completed within about three minutes thereafter. At such time, the product may be size reduced, using a micropulverizer or Entoleter impact machine or other equivalent or similarly useful apparatus. If desired, hydratable salt, such as trisodium phosphate, may then be added to the mixer to take up any excess water present and possibly, to help stabilize the bleaching material and perfume against decomposition due to the presence of the moisture. The proportion of salt present should be sufficient to tie up all the moisture present to prevent it from entering into undesirable reactions. In a preferred operation, the addition of detergent acid will take about 4 to 6 minutes, the addition of water may take from 0 to 2 minutes after completion of addition of the acid and calcium carbonate, after completion of moisture spraying and reagent additions about 0.5 to 2 minutes will be allowed to complete mixing and then, in about 0.2 to 1 minute, trisodium phosphate, colorant and colored detergent particles or other suitable adjuvants will be added and about 0.5 to 3 minutes will be allowed for the hydratable salt to absorb any free moisture. At this point, chlorinated cyanuric acid bleach will be blended in, over a period of about 0.2 to 1 minute, followed by spraying in of perfume, which may take from 1 to 4 minutes. As soon as the perfume has been added the product may be size reduced. Thus, the entire operation for the manufacture of a finished scouring cleanser, may take only about 20 minutes, including neutralization of the detergent acid, and the time for size reducing, which may be about 4 to 6 minutes. It is found that the speed of production of scouring cleanser is essentially the same as that for cleansers containing already neutralized and dry detergent material.

The ribbon mixer employed, a Day mixer, is one having a cut-out center discharge ribbon agitator made of carbon steel and turning at 25 to 100 revolutions per minute. The centrifugal impact mill, preferably of the Entoleter type, Series 27, belt driven and of abrasion-resistant construction, is operated at 2,000 to 3,000 r.p.m. The perfume spraying system is an ordinary spray nozzle located at the top of the ribbon blender and capable of spraying the perfume onto the detergent in finely divided globules. The spraying system may be employed for wetting the calcium carbonate for reaction with detergent acid.

In the preparation of the cleanser the detergent acid turns whitish within three minutes of the addition of the water and becomes sweet smelling, indicating neutralization has been effected. When no water is used, the time of neutralization may be as long as an hour or more and the product is sometimes discolored. When, instead of following the present method, sodium alkyl benzene sulfonate of the same type is employed, except for the presence of sodium instead of calcium in the detergent salt, foaming

of the cleanser and associated cleaning effectiveness are measurably diminished. It has been found that the present compositions, including calcium detergent salt, are approximately 50% more effective than similar compositions based on sodium detergents. For example, when 3.7% of active detergent, sodium salt, is replaced by 2.5% of active detergent, calcium salt, made according to this invention, the foaming power of the invented product is better and it is as good in cleaning or better than "standard" product containing sodium detergent salt. Thus, the invented products are more economical, easier to manufacture and superior to those previously known.

Among the savings made utilizing present methods is the saving of heat for a spray dryer, the saving of capital investment in a spray dryer and the saving in the expenses of conveying and storage facilities for spray dried product to be charged to a mixer. No classifier is needed and the only additional piece of equipment employed is a grinder or size reducer, which is often used in a detergent or cleanser factory anyway. In the normal scouring cleanser plant of commercial size savings effected are in the hundreds of thousands of dollars per year. And a better product is obtained.

Various improvements may be made in the described process and are within the invention. Thus, by improving the spray techniques, small "lumps" of neutralized detergent will be produced and throughput of the grinder may be increased. In a similar manner, it will be apparent to one of skill in the art what other changes may be made in the present invention to adapt it for utilization with particular materials, to improve efficiency of operations and to make better products. Such changes, insofar as they are taught or suggested by the present specification and are within the inventive concept, are considered to be part of the present invention.

The following examples illustrate the invention. They are not to be considered as limiting it. Unless otherwise indicated, all parts are by weight and all temperatures are in ° C.

EXAMPLE 1

Dodecyl benzene sulfonic acid analyzing 88% of the mentioned detergent acid (derived from propylene tetramer), 8.2% of sulfuric acid, from sulfonation with fuming sulfuric acid, about 1% free oil, mostly the corresponding alkyl benzene, and about 2.8% water is neutralized in a Day ribbon mixer with powdered calcium carbonate, obtained by crushing and pulverizing limestone. The calcium carbonate is anhydrous and of a finely divided particulate nature, substantially all of it passing through a 140 mesh sieve, U.S. Standard Sieve Series, and most of that passing through a 200 mesh sieve. 395 parts of the detergent acid mix upper layer are reacted with 9,143 parts of the calcium carbonate. The yield of neutralized product, including calcium sulfate, free oil and water, is about 9,500 parts, with about 36 parts lost due to evolution of carbon dioxide.

About ¼ of the calcium carbonate is added to a Day ribbon mixer, having a carbon steel ribbon or blade turning at about 50 r.p.m. Then, with the mixer operating, the detergent acid and the rest of the calcium carbonate powder are added together, over a period of about five minutes, after which water is atomized onto the mixing powder by a spray nozzle inside the mixer, at the top center thereof. In the mixing-spraying operation the wet contact loci formation is effected within about one minute, and within an additional minute neutralization of the detergent acid is completed, as is evidenced by a milky white appearance of the detergent salt and the disappearance of a sour odor. The proportion of water sprayed onto the mixing calcium carbonate and detergent acid is about 0.4% of the end product or about 10% of the crude sulfonic acid from the detergent acids upper layer. The particle sizes of the globules of water sprayed average from 10 to 100 microns in diameter. With water addition, as described, the time passing between addition of reactants

to completion of neutralization is less than ten minutes and most of that is taken up by the additions of the reagents rather than by the reaction itself.

After the neutralization is completed there are added to the calcium detergent salt-calcium carbonate mixture in the sequence described, 300 parts of anhydrous trisodium phosphate, 72 parts of coloring material, 72 parts of colored detergent beads of about 1 millimeter diameter, 30 parts of trichlorocyanuric acid and 25 parts of perfume for the scouring cleanser. The trisodium phosphate, dye and color dots are added together over about 1/2 minute after mixing for a minute after water spraying. Mixing is continued for another minute and trichlorocyanuric acid is added, possibly alone or with some calcium carbonate, the calcium carbonate being employed to clear the mixer addition chute of bleach. Any calcium carbonate so added is subtracted from the charge thereof for neutralization. After completion of the addition of the bleach the perfume is sprayed in from the mixer top, in droplets of approximately 50 to 100 microns average diameters, over a 2.5-minute period. As soon as perfume addition is completed the product is fed to a high speed impact size reducing machine, an Entoleter mill of the centrifugal type. Series 27, belt driven, with a 24-inch diameter rotor rotating at 2,500 r.p.m. The mill reduces the comparatively small lumps of neutralized detergent and any other over-size particles to an extent that the product substantially all passes through a 140-mesh sieve, with most of the particles being from 100 to 200 mesh. If desired, the colored particles of detergent or builder mix, added to the product for distinctiveness of appearance, may be post added to the cleanser after size reduction, so that they will still be of maximum size and readily identifiable.

The product made is an excellent scouring cleanser, of excellent cleansing, foaming and bleaching properties. It is stable on storage, compared to a similar product in which dry neutralized detergent sodium salt is charged and it is superior to such a product in foaming and deterative powers. In addition, the improved properties are obtained without the need for spray drying the detergent, the above operations being undertaken at room temperature, approximately 25 to 30° C.

When, instead of the 3.7% level of synthetic organic detergent in the cleanser, the contact of detergent is cut 50%, to 2.5%, the product is still as good in foaming and cleaning power as the comparable cleanser based on sodium detergent at a 3.7% level. Generally, this superiority is obtained or obtainable when other scouring materials are blended in with the calcium carbonate, e.g., silex of comparable particle sizes, providing that the calcium carbonate is at least 25% of the scouring material content, preferably at least 50% thereof. Such conditions prevail when the proportions of detergent acid, calcium carbonate and other mentioned ingredients are varied over the ranges previously set forth.

Analysis of the finished product indicates that the detergent is in the form of the calcium double salt but the useful results are also obtained when the "acid salts," in which the detergent is only partly neutralized with calcium and is partly neutralized with sodium or other cation (magnesium is more preferable). However, it is important that complete neutralization is effected, to avoid having a poorly flowing product. In this respect, the low active ingredient products, having only from 1.5 to 3% of synthetic detergent, are freer flowing than the comparable higher A. I. materials.

By following the procedures of the invention, using other detergents of the types named and taught, other builders and various adjuvants, essentially the same improvements in processing and end products are obtained, providing that the calcium carbonate neutralizing agent is employed.

What is claimed is:

1. A process for the manufacture of a scouring cleanser

composition which comprises neutralizing an essentially dry acid form of water soluble organic detergent consisting essentially of water soluble anionic detergent with a large excess of water insoluble scouring material containing at least 25% calcium carbonate in the presence of a minor proportion of water on loci of contacts of the detergent acid and calcium carbonate, and wherein calcium carbonate is at least 25% of the scouring material and at least 20% of the final scouring cleanser composition, the detergent acid is from 0.5 to 5% of the final cleanser composition and the calcium carbonate is from 500 to 20,000 percent of the detergent acid.

2. A process according to claim 1 wherein neutralization is effected by admixing of an essentially dry, liquid, acid form of the synthetic organic detergent component and water insoluble scouring material to produce water soluble detergent, while spraying onto the surfaces of the particles of the mixture a minor proportion of water.

3. A process according to claim 2 wherein the calcium carbonate is at least 50% of the scouring material substantially all of which passes through a 200 mesh sieve, the synthetic organic detergent acid is a C₁₂-C₁₈ benzene sulfonic acid which contains less than 10% water.

4. A process according to claim 3 wherein the benzene sulfonic acid is a C₁₂-C₁₅ benzene sulfonic acid containing from 0.1 to 5% of water and 0.1 to 10% of sulfuric acid, at least some of the calcium carbonate is added to the mixing zone before the detergent acid and the water sprayed on is from 0.1 to 3% of the product.

5. A process according to claim 4 wherein the scouring material in the scouring cleanser is powdered calcium carbonate or a mixture of such material and powdered silica, the alkyl of said detergent acid is either branched or linear, the water content of the detergent acid is from 0.5 to 3% thereof and the water sprayed onto the calcium carbonate and detergent acid reactants in the mixer is from 0.1 to 0.5% of the product.

6. A method according to claim 4 wherein mixing takes place in a ribbon mixer, the water sprayed onto the mixing calcium carbonate and detergent acid is atomized to particle sizes which average in the range of from 5 to 100 microns, size reduction of the scouring cleanser is effected in a high speed impact mill, and after size reduction the product is packaged without additional screening or classification treatments.

7. A process according to claim 5 wherein builder salt capable of taking up moisture from the neutralized reaction mixture is added to the neutralized composition in an amount of from 1 to 5% of the composition.

8. A process according to claim 7 wherein the hydratable builder salt is a phosphate capable of being hydrated and thereby sorbing water from the scouring cleanser, and the bleach is a chlorinated cyanuric acid.

9. A process according to claim 5 wherein oxygen or chlorine liberating bleaching agent is added to the neutralized composition in an amount of from 0.1-2% of the composition.

10. A Process according to claim 7 wherein perfume is added to neutralized composition in an amount of from 0.5-1% of the composition.

11. A process according to claim 8 wherein the higher alkyl benzene sulfonic acid is a propylene tetramer benzene sulfonic acid, the phosphate is trisodium phosphate and the bleach is trichlorocyanuric acid.

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